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A LABORATORY MODEL SYSTEM FOR DETERMINING THE VOLATILITY OF PESTICIDES FROM SOIL AND PLANT SURFACES

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ABSTRACT
A laboratory model system for the direct determination of the volatilization of pesticides from soil and plant surfaces has been developed. Experiments have been carried out with lindane and atrazine as test substances, a light "sandy soil" and a "peat soil" as test soils, oats (Avena sativa L.), bean (Phaseolus aureus L.), and turnip (Brassica rapa L.) as test plants, and varying temperatures and soil moisture contents. The half-lives were strongly dependent on soil type, soil humidity, and soil temperature, or plant species and leaf temperature, resp.

INTRODUCTION

Volatilization plays an important role in the dispersion of pesticides in the environment. For persistent pesticides which are very slowly degraded by biotic and abiotic mechanisms, volatilization is the major pathway for the decrease of pesticide residues in plants and soil. Volatilization also leads to a rapid transport and distribution of pesticides in the atmosphere, resulting in considerable wet and dry deposition. For example, in Bavaria lindane was measured in rain water in average concentrations of 83 ng/l (maximum 400 ng/l [1]). At various locations in California, a total of 17 pesticides and other organic contaminants was found in fog water (atrazine: concentrations of 270-820 ng/l [2]). Thus, even pesticides with low vapour pressure are transferred to the atmosphere by volatilization processes.

Since volatilization is an important factor in the fate of pesticides in the environment, it is necessary to have an experimental design to measure this process. Various laboratory model systems for direct and indirect determination of volatilization of pesticides from treated surfaces are described in literature. The indirect methods estimate the volatility losses by measuring the remaining pesticide concentrations on water, soil, metal or glass surfaces. However, an exact determination of volatilization of pesticides can be achieved only by direct measurement of volatilization rates using some means of trapping the vaporized pesticide. By direct measurements the volatilization of pesticides from glass [3-7], water [4,8,9-10], soil [4,6,8,10-12] and plant [3,6-7,13] surfaces was determined.

In this work, a simple laboratory model system for the direct determination of the volatilization of pesticides from soil and plant surfaces is reported.

MATERIALS AND METHODS

Description of the Volatilization Model System

Volatilization chamber: The volatilization chamber permits the realization of both soil and plant experiments. The special design of the air inlet and outlet funnels including relatively wide tubes for both incoming and leaving air guarantees a nearly laminar air stream within the chamber. The air inlet funnel contains three sieves in series (fig. 1). The sieves are made of plastic curtain cloth (max. inside diameter of the lattice 0.5 mm), fixed in the inlet funnel. Two of the sieves are located in the middle of the inlet funnel. The distance between them is 1 cm. The third sieve serves as last barrier between inlet funnel and volatilization chamber.

Within the chamber, both the incoming and the leaving air stream are passing over 7.4 cm Teflon plate covered calming zones before entering and after leaving the test area, to reassure air stream laminarity in the test region. The volatilization chamber (fig. 2, l= 400 mm, w= 137 mm, h= 277 mm) and the air outlet funnel are made of DURAN glass plates fixed together with a 2-component glue (epoxy resin UHU PLUS ENDFEST 300, UHU, D-8560 Bühl). The glass plate at the top of the chamber contains two orifices fitted with glass thread runouts, allowing the introduction of a hygrometer and a surface thermometer. The outer metal frame of the chamber guarantees the stability of the inner glass plate construction and makes it possible to flange the aluminum air inlet funnel to the open right small side of the chamber.

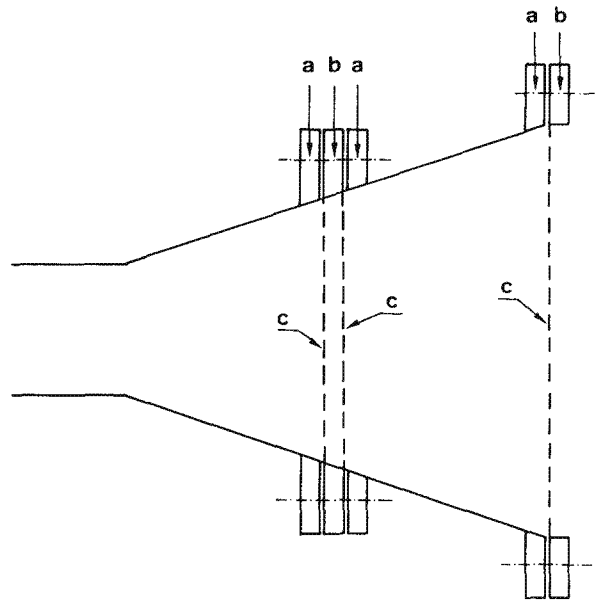


Fig. 1: Air Inlet Funnel

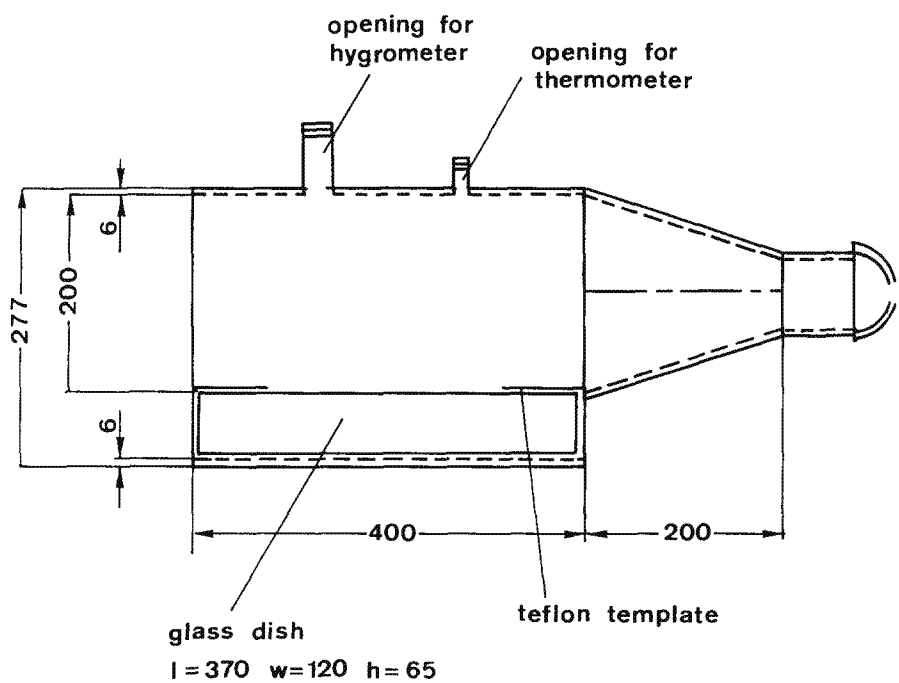


Fig. 2: Volatilization Chamber

This right open side permits the change of the test substrates and the cleaning of the inner glass walls of the volatilization chamber by irrigation. The soil or the plants are put in a rectangular glass bowl (l= 370 mm, w= 130 mm, h= 60 mm) which is introduced into the chamber. The glass bowl is then covered with a Teflon template with the inner dimensions of the chamber, with an inner rectangular hole, to avoid air turbulences resulting from the small gaps between the glass bowl and the chamber walls, and to build up the calming zones in front of and behind the test area. The test area is limited by the dimensions of the rectangular hole in the Teflon template (l= 240 mm, w= 108 mm). In the soil experiments a Teflon table made of two Teflon blocks and a Teflon plate, with the inner dimensions of the glass bowl, is introduced in the glass bowl before filling the soil in, thus reducing soil layer depth to 1 cm. On occasion of the plant experiments, plants that have been previously cultivated in cultivation pots (PE, l= 39 mm, w= 34 mm, h= 60 mm) are placed directly into the glass bowl, keeping them in their cultivation pots.

Before beginning the experiments, air stream laminarity was confirmed by determining the air velocity behind the air inlet tunnel at 1 cm intervals over the total air stream area.

The difference between the air pressure in the chamber during the experiments and the ambient atmospheric pressure was very low (30 - 40 mbar less in the chamber).

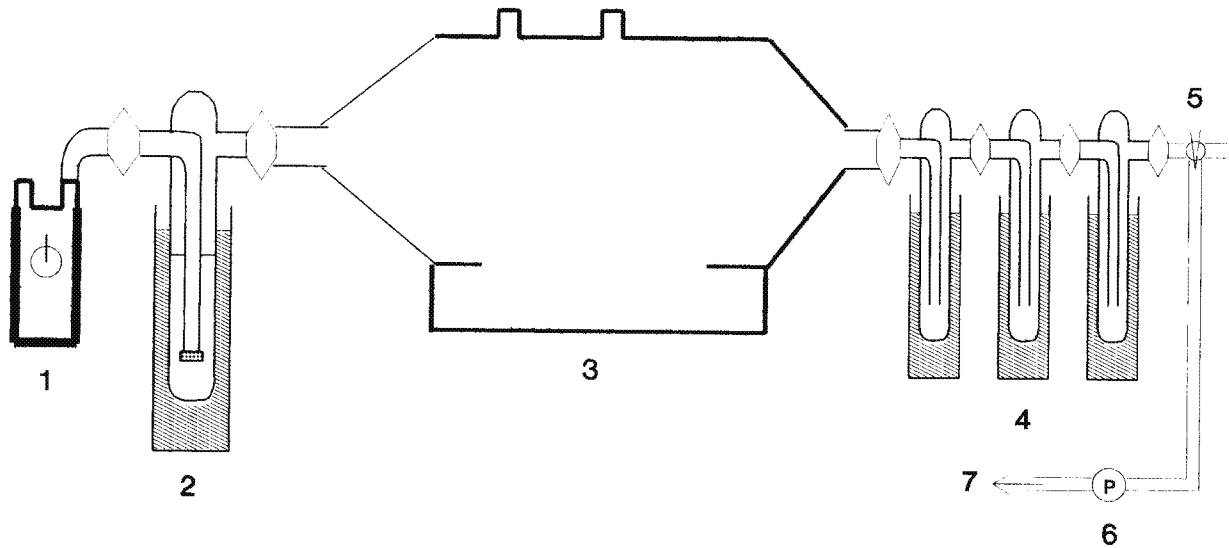
Test system: The laboratory model system for determination of the volatilization of pesticides from soil and plant surfaces is shown in fig. 3.

Other Apparatus Used

Air velocity and stream laminarity were determined by a thermic anemometer (Lambrecht, model 642).
Liquid scintillation counter: Berthold, BF 8000; external standardization
Sample oxidizer: Packard, B 306.
Gaschromatograph: Dani 8500, integrator: Shimadzu C-R3A

Reagents

Lindane and atrazine were purchased from Celamerck, Ingelheim and Ehrenstorfer, Augsburg respectively. C-14-labeled lindane and atrazine were purchased from Amersham Buchler, Braunschweig. The solvents (acetone, methanol, ethylacetate) were analytical grade (Merck, Darmstadt). For application lindane was dissolved in acetone and atrazine in methanol.



1 - gas meter
2 - gas washing bottle
3 - volatilization chamber
4 - cooling traps
5 - regulation valve
6 - pump
7 - air outlet

Fig. 3: Apparatus to Determine Volatilization Rates of Pesticides from Soil or Plant Surfaces

As scintillation liquid, Hydroluma (J.T. Baker B.V., Deventer, Holland) was used.

For solid-phase extraction of the aqueous solutions, Bond elut columns, Octadecyl C18, 500 mg/2.8 ml (Analytichem International) were used.

Soils and Plants

Two soil types with different clay and organic matter content (table 1) were selected.
Before beginning the experiment, soil moistures were kept at the air dry level or brought to 40 % of the maximal water holding capacity by adding distilled water. Maximal water holding capacity of the soils was determined by the method of Nehring [14].

For the plant experiments, three different plant species were used: oats (Avena sativa L.), bean (Phaseolus aureus L.), and turnip (Brassica rapa L.). At the beginning of the experiment, oats and beans were 10 days old and turnip 15 days.

Table 1: Analysis of the Soils

Properties	sandy soil	peat soil
pH ($CaCl_2$)	6.5	5.9
Clay < 2 µm [%]	7	31
Silt 2 - 63 µm [%]	26	40
Sand 0.063 - 2 mm [%]	67	29
Total organic matter content [%]	1.9	20.6
Total C - content [%]	1.1	12.0
Maximal water holding capacity (% weight of dry soil)	36.4	130.0
Volume weight [g/l]	1200	780
Dry residue [%]	99.1	91.2
Density [g/ml]	2.57	1.92
Porosity:		
Total pore space [%]*	53.7	70.0
Wide coarse pores [%]*	19.7	26.2
Narrow coarse pores [%]*	9.9	5.5
Medium pores [%]*	10.2	6.7
Fine pores	6.8	31.2

* in % of total soil volume

Procedure

The air-dried or moist soils were spread on top of the Teflon table inside the rectangular glass bowl. The bowl was introduced into the volatilization chamber and capped with the Teflon template. Then the pesticides were applied evenly on the test area by dropping with a Hamilton syringe. The plants in their cultivation pots were placed in the glass bowl. The pesticide solution was applied to the plant surfaces by means of a brush.

The pesticides were applied to the soil and plant surfaces in amounts which are common in agricultural practice [15], except for atrazine in the plant experiments. On the plant surfaces the applied atrazine was 15 % of the common amount.

After application the air inlet funnel was fitted to the volatilization chamber and the experiment was started by sucking air through the model system. The air stream was kept at a constant speed of 0.05 m/s. Air humidity (> 98 %) and the temperature on soil or plant surfaces were measured and controlled. In general the experiments were carried out at 10°C and 20°C.

The cooling traps were changed at defined time intervals, in general every 1 or 2 hours. Samples were taken at minimum 5 times per test run. In general, the experiments were run for 1 day. Soil moisture did not change during this time span. For quantification of the vaporized pesticides the cooling traps as well as the chamber walls were rinsed with water and the pesticides were extracted from the aqueous solution by solid phase extraction. The extracts were analysed by gas-liquid chromatography. For the quantitative description of the volatility of pesticides from soil and plant surfaces, the half-life concept was used.

All experiments were carried out in duplicates. In preliminary tests a mass balance was made to exclude undesirable losses in the system. In some experiments, especially in the mass balance tests, radioactive pesticides were used. Total ^{14}C recoveries were 101.3 % $\pm$ 3.7 for lindane and 103.0 % $\pm$ 2.0 for atrazine.

GASCHROMATOGRAPHIC CONDITIONS

A) For lindane the gaschromatographic conditions were as follows. Detector: ^{63}Ni-ECD; column: DB5(30m), 0.32 mm i.D., film thickness 0.25 mm; carrier gas: nitrogen 4.5 ml/min; make up gas: nitrogen 70 ml/min; injector temperature: 260°C: detector temperature 260°C; column temperature: 70°C (1 min isothermal), to 140°C with a rate of 30°C/min, to 240°C with a rate of 7°C/min, 240°C (4 min isothermal).

B) For atrazine, the following conditions were used. Detector: phosphor-nitrogen-detector; column: DB5(30 m), 0.32 mm i.D., film thickness 0.1 µm; carrier gas: helium 4.2 ml/min; make up gas: nitrogen 16 ml/min; hydrogen: 23 ml/min; air: 180 ml/min; injector temperature: 250°C; detector temperature: 250°C; column temperature: 60°C (0.7 min isothermal), to 140°C with a rate of 30°C/min, to 250°C with a rate of 10°C/min, 250°C (5 min isothermal).

RESULTS

Volatilization of Lindane and Atrazine from Soil Surfaces

In the case of atrazine the experiments were conducted at 20°C only, because of the low vapour pressure (10^{-5} Pa) of the substance.

The half-lives determined for lindane varied in a range of 2.7-22.2 days and the half-lives of atrazine were in a range of 143-> 1000 days (table 2). For both substances the half-lives were strongly dependent on soil type and soil moisture. Lindane also showed a correlation between half-life and temperature.

In moist peat soil, the halflives of lindane and atrazine were much higher than in moist sandy soil, whereas in dry peat soil the half-lives of the pesticides were lower than in dry sandy soil. The half-lives of lindane and atrazine were enhanced by adding water to peat soil. However, in sandy soil increasing water content led to decreasing half-lives of lindane and atrazine.

In both soils the half-lives of lindane decreased with increasing soil temperature.

There are some half-lives of lindane on soil reported in literature. On moist fallow soil, the half-lives varied between 0.3 days in field experiments [16] and 1-4 days in a microagroecosystem [17]. In laboratory tests the half-life of lindane was found to be 0.7 days [18] and with the Dow-method it was calculated to be 3.4 days [18]. However, it is very difficult to compare literature data with the half-lives found in this study because the data taken from literature lack of detailed information about soil humidity, soil composition and, partially, even about soil temperature.

Volatilization of Lindane and Atrazine from Plant Surfaces

Experiments with Phaseolus aureus were made only at 20°C, because at 10°C this plant cannot be kept.

The half-lives determined were in a range of 0.31-0.68 days for lindane and 14.6-53.4 days for atrazine (table 3). As in case of volatilization from soil surfaces, the half-lives of atrazine on plant surfaces are longer than those of lindane. On plant surfaces, also, half-lives were negatively correlated with temperature. For both pesticides the half-lives were longer on bean and turnip than on oat leaf surfaces.

Literature data of volatilization rates of lindane from plant surfaces[3] are not directly comparable to our data because of the different temperatures.

Table 2: Half-lives of Volatilization of Lindane and Atrazine from Soil Surfaces (relative air humidity > 98 %, wind velocity 0.05 m/s)

Pesticide	Soil type	Soil humidity (% MWC)*)	Temperature (°C)	Half-life (days)
Lindane	peat soil	air dry	10 ± 1	11.6
	peat soil	40	10 ± 1	22.2
	sandy soil	air dry	10 ± 1	21.5
	sandy soil	40	10 ± 1	4.7
	peat soil	air dry	20 ± 1	5.5
	peat soil	40	20 ± 1	15.9
	sandy soil	air dry	20 ± 1	6.7
	sandy soil	40	20 ± 1	2.7
Atrazine	peat soil	air dry	20 ± 1	655
	peat soil	40	20 ± 1	> 1000
	sandy soil	air dry	20 ± 1	939
	sandy soil	40	20 ± 1	143

*) percent of maximal water holding capacity

Nevertheless, it seems that the volatilization rates of lindane from the leaf surfaces of garden beans (Phaseolus vulgaris) found by Starr and Johnson[3] are clearly lower than the volatilization rates of lindane from Phaseolus aureus found in our study. Starr and Johnson[3] found that the loss of lindane from garden bean surfaces after 96 hours was 21-23.9% of the applied amount at 16°C and 58.1-70.6% at 27°C. The rate of loss from bean leaves was linear at 16°C throughout the 96-hour period. At 27°C, however, the rate was approximately linear up to 72 hours, after which the loss occurred at a diminishing rate.

Table 3: Half-lives of Volatilization of Lindane and Atrazine from Plant Surfaces (rel. air humidity > 98 %; wind velocity 0.05 m/s)

Pesticide	Plant	Leaf temperature (°C)	Half-life (days)
Lindane	Turnip (Brassica rapa)	11 ± 1	0.68
	Oats (Avena sativa)	11 ± 1	0.59
	Bean (Phaseolus aureus)	20 ± 1	0.56
	Turnip	20 ± 1	0.40
	Oats	20 ± 1	0.31
Atrazine	Oats	10 ± 1	53.4
	Bean	20 ± 1	25.6
	Turnip	20 ± 1	24.3
	Oats	20 ± 1	14.6

DISCUSSION

The half-life times obtained from these short-term studies are valid only for the first time period after application. Nevertheless, these experiments show that even low volatile pesticides such as atrazine have measurable volatilization rates from soil and plant surfaces and, thus, may contribute to an unwanted contamination of the air where they can be measured, for example, in rain and fog water [1,2].

The qualitative interpretation of the conducted experiments clearly shows the influences and significances of the different experimental parameters on pesticide volatilization. The half-lives of the studied pesticides were found to be strongly dependent on soil type, soil humidity, and soil temperature, or plant species and leaf temperature, resp.

In several studies in literature [12, 19-20] the authors found that the volatility of various pesticides decreases with increasing organic matter content in the soil. For weak polar, non ionic pesticides the soil organic matter content is the most important factor for adsorption [21], which is negatively correlated with volatilization.

For moist soils our results are in agreement with literature data. However, on air-dry soils the situation is reversed: on air-dry peat soil, lindane and atrazine have higher volatility rates than on air-dry sandy soil. In an air-dry state the adsorption capacity of peat soil seems to be lower than that of

sandy soil in spite of its higher organic matter content.

Concerning the influence of soil humidity on volatilization of pesticides, again, our results for sandy soil are in accordance with literature; however, our results for peat soil are in contrast to literature data. Several authors reported that pesticides evaporate more rapidly from moist soils than from dry soils [17, 19-23], because water molecules compete for adsorption sites on the soil. For non-polar and weakly polar compounds, water is preferentially sorbed onto soil particles, thus displacing the chemical. However, in our work, in the case of peat soil the volatilization rates of lindane and atrazine are higher on dry soil than on moist soil. This fact cannot be explained by the above theory. For explaining the exceptional behaviour of peat soil further research is needed.

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